

JUN 05 2007

FACSIMILE TRANSMITTAL FORM	Application Number	10/689,172
	Confirmation Number	2716
	Filing Date	October 20, 2003
	First Named Inventor	Lunsford, Duane A.
	Examiner Name	Daniel R. Zirker
Fax: 571-273-8300	Attorney Docket Number	58683US003
Total Number of Pages in This Submission: 27		
Date: JUN 05 2007	Attorney for Applicant: Thomas M. Spielbauer/kmm	

ENCLOSURES (check all that apply)		
<input type="checkbox"/> Fee Transmittal Form <input type="checkbox"/> Issue Fee Transmittal <input type="checkbox"/> Amendment Transmittal	<input type="checkbox"/> Petition	<input type="checkbox"/> Appeal Communication to Board of Appeals and Interferences
<input type="checkbox"/> Amendment/Reply <input type="checkbox"/> After Final <input type="checkbox"/> Affidavits/Declaration(s)	<input type="checkbox"/> Petition to Convert a Provisional Application	<input type="checkbox"/> Appeal Communication to Technology Center (Appeal Notice, Brief, Reply Brief)
<input type="checkbox"/> Extension of Time Request	<input type="checkbox"/> Power of Attorney, Revocation	<input type="checkbox"/> Proprietary Information
<input type="checkbox"/> Express Abandonment Request	<input type="checkbox"/> Change of Correspondence Address	<input type="checkbox"/> Status Letter
<input type="checkbox"/> Information Disclosure Statement	<input type="checkbox"/> Terminal Disclaimer	<input checked="" type="checkbox"/> Other Enclosures: Amended Brief on Appeal
<input type="checkbox"/> Response to Missing Parts/Incomplete Application <input type="checkbox"/> Response to Missing Parts under 37 CFR § 1.52 or 1.53 <input type="checkbox"/> Response to Missing Parts under 35 USC 371 in US Designated/ Elected Office (DO/EO/US)	<input type="checkbox"/> Request for Refund	
	<input type="checkbox"/> Request for Continued Examination (RCE) Transmittal	
<input type="checkbox"/> Drawings	<input type="checkbox"/> After Allowance Communication to Technology Center	

THE INFORMATION CONTAINED IN THIS FACSIMILE TRANSMISSION
MAY CONTAIN CONFIDENTIAL OR LEGALLY PRIVILEGED INFORMATION
INTENDED ONLY FOR THE PERSON OR ENTITY NAMED BELOW.

If you are not the intended recipient, please do not read, use, disclose, distribute or copy this transmission.
If this transmission was received in error, please immediately notify me by telephone directly at 651-736-9814 or 651-733-1500, and we will arrange for its return at no cost to you.

JUN 05 2007

32692

Customer Number

Patent
Case No.: 58683US003**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

First Named Inventor: LUNSFORD, DUANE A.
Application No.: 10/689,172 Group Art Unit: 1771
Filed: October 20, 2003 Examiner: Daniel R. Zirker
Title: ADHESIVE ARTICLES INCLUDING NANOPARTICLE PRIMER AND
METHODS FOR PREPARING SAME

AMENDED BRIEF ON APPEAL

Mail Stop: Appeal Brief-Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

CERTIFICATE OF MAILING OR TRANSMISSION [37 CFR § 1.8(n)] I hereby certify that this correspondence is being: <input type="checkbox"/> deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450. <input checked="" type="checkbox"/> transmitted by facsimile on the date shown below to the United States Patent and Trademark Office at 571-273-8300. JUN 05 2007 Date Signed by: Kathleen M. Murray
--

Dear Sir:

This is an appeal from the Office Action mailed on October 28, 2005, in light of the Advisory Action mailed January 6, 2006, finally rejecting claims 1-11 and 29-37.

A Notice of Appeal in this application was mailed on February 28, 2006, and was received in the USPTO on March 6, 2006.

A Brief on Appeal was filed May 8, 2006. A Reply Brief was filed on July 20, 2006.

This Amended Brief on Appeal is filed in response to a Notification of Non-Compliant Appeal Brief sent electronically on May 10, 2007.

Applicants' submissions to the Board include both this Amended Brief on Appeal, as well as the Reply Brief filed on July 20, 2006.

It is believed that no fee is required. However, any fee should be charged to Deposit Account No. 13-3723.

JUN 05 2007

Application No.: 10/689,172

Case No.: 58683US003

TABLE OF CONTENTS

Real Party In Interest.....	3
Related Appeals And Interferences.....	3
Status of Claims.....	3
Status of Amendments.....	3
Summary Of Claimed Subject Matter.....	4
Grounds of Rejection to be Reviewed on Appeal.....	5
Argument.....	6
I. Claims 1-11 and 29-37 stand rejected under 35 U.S.C. § 103(a) as purportedly being unpatentable over Lange et al. (US 4,816,333).....	6
A. At best, Lange et al. might pique a scientist's curiosity to investigate further, but the disclosure of Lange et al. does not contain a sufficient teaching that the claimed result would be achieved.	6
B. EP '756 clearly and unambiguously steers one of ordinary skill in the art to the use of primers containing nanoparticles modified by ambifunctional silanes, rather than primers consisting essentially of nanoparticles.....	7
C. The Examiner has failed to establish the requisite reasonable expectation of success, and for at least this reason, the rejection should be reversed.	9
II. Claims 6 and 32 stand rejected under 35 U.S.C. § 103(a) as purportedly being unpatentable over Lange et al., in view of Melancon et al. (US 2003/0152768 A1).....	9
Conclusion.....	10
Claims Appendix.....	11
Evidence Appendix.....	14
Murray Declaration.....	15
EP 0 372 756.....	16
Related Proceedings Appendix.....	None

Application No.: 10/689,172

Case No.: 58683US003

REAL PARTY IN INTEREST

The real party in interest is 3M Company of St. Paul, Minnesota and its affiliate 3M Innovative Properties Company of St. Paul, Minnesota.

RELATED APPEALS AND INTERFERENCES

Appellants are unaware of any related appeals or interferences.

STATUS OF CLAIMS

Claims 1-11 and 29-37 are pending.

Claims 12-28, and 38 were cancelled.

Claims 1-11 and 29-37 stand rejected and are the claims on appeal.

STATUS OF AMENDMENTS

Applicants filed an after final response under 37 C.F.R. § 1.116 mailed December 20, 2006, which included a request to cancel claim 38. According to the Advisory Action mailed January 6, 2006, the request to cancel claim 38 was entered. No other after-final amendments were made.

Application No.: 10/689,172

Case No.: 58683US003

SUMMARY OF CLAIMED SUBJECT MATTER

Generally, an adhesive article comprises a substrate having an adhesive applied to at least a portion of at least one surface of the substrate. Examples of such adhesive articles include single-coated and double-coated adhesive tapes, including foam tapes. There are numerous methods for treating substrate surfaces to improve the adhesion of adhesives thereto, such as chemical etching, electron-beam irradiation, corona treatment, plasma etching, coextrusion of adhesion promoting layers, and coating substrates with adhesion promoting primer coatings, some of which may be subsequently crosslinked. The desired result of these adhesion-promoting methods is to make the substrate more receptive to adhesives and to promote strong interfacial bonds between the substrate and the adhesive. There is a continuing need to identify improved materials and methods for increasing the adhesion between substrates and adhesives. (See page 1, lines 14 – page 2, line 7.)

The claims of the present application concern adhesive articles and methods of bonding an adhesive layer to a substrate that include a primer that consists essentially of nanoparticles. Referring to FIG. 1, exemplary adhesive article 10 comprises substrate 14 having first surface 24, and adhesive layer 12 having first surface 22. First surface 22 of adhesive layer 12 is bonded to first surface 24 of substrate 14 such that primer 16 is interposed between adhesive layer 12 and substrate 14. (See page 3, lines 8-11.)

Exemplary substrates include polymeric films and foams, as described at, e.g., page 3, line 27 – page 8, line 9. Exemplary adhesives are described at, e.g., page 8, line 10 – page 11, line 19, and include, e.g., pressure-sensitive and non-pressure sensitive adhesives, acrylate and methacrylate polymers and copolymers, and silicone pressure sensitive adhesives. The adhesive layer comprises no more than 3% by weight acrylic acid repeat units. (See, e.g., page 11, lines 8-10, and independent claims 1 and 29.)

The primer consists essentially of nanoparticles, wherein the term “consists essentially of” has been expressly defined to mean “free of an effective amount of a component that reacts with the adhesive or the substrate (i.e., ambifunctional silane), and /or any polymeric binders that act to increase the adhesion of the adhesive to the substrate.” (See page 11, lines 20-23.)

Exemplary nanoparticles are described at, e.g., page 11, line 24 – page 14, line 11.

Application No.: 10/689,172

Case No.: 58683US003

GROUND OF REJECTION TO BE REVIEWED ON APPEAL

- I. Claims 1-11 and 29-37 stand rejected under 35 U.S.C. § 103(a) as purportedly being unpatentable over Lange et al. (US 4,816,333).
- II. Claims 6 and 32 stand rejected under 35 U.S.C. § 103(a) as purportedly being unpatentable over Lange et al., in view of Melancon et al. (US 2003/0152768 A1).

Application No.: 10/689,172

Case No.: 58683US003

ARGUMENT**I. Claims 1-11 and 29-37 stand rejected under 35 U.S.C. § 103(a) as purportedly being unpatentable over Lange et al. (US 4,816,333).**

“The consistent criterion for determination of obviousness is whether the prior art would have suggested to one of ordinary skill in the art that this process should be carried out and would have a reasonable likelihood of success, viewed in the light of the prior art.” (In re Dow Chemical Co., 837 F.2d 469, 473, 5 USPQ2d 1529, 1531 (Fed. Cir. 1988) (internal citations omitted).) “A critical step in analyzing the patentability of claims pursuant to section 103(a) is casting the mind back to the time of invention, to consider the thinking of one of ordinary skill in the art, guided only by the prior art references and the then-accepted wisdom in the field.” (In re Kotzab, 217 F.3d 1365, 1369, 55 USPQ2d 1313, 1316 (Fed. Cir. 2000).) “That the inventors were ultimately successful is irrelevant to whether one of ordinary skill in the art, at the time the invention was made, would have reasonably expected success. [A] finding to the contrary represents impermissible use of hindsight-using the inventors' success as evidence that the success would have been expected.” (Life Technologies, Inc. v. Clontech Laboratories, Inc., 224 F.3d 1320, 1326, 56 USPQ2d 1186, 1191 (Fed. Cir. 2000) (internal citations omitted).)

The test for obviousness requires evaluation of “the references as a whole so that their teachings are applied in the context of their significance to a technician at the time....” (See, e.g., Interconnect Planning Corp. v. Feil, 744 F.2d 1132, 1143, 227 USPQ 543, 551 (Fed. Cir. 1985).) “When prior art contains apparently conflicting references, the Board must weigh each reference for its power to suggest solutions to an artisan of ordinary skill.” (In re Young, 927 F.2d 588, 591, 18 USPQ2d 1089, 1091 (Fed. Cir. 1991).)

A. *At best, Lange et al. might pique a scientist's curiosity to investigate further, but the disclosure of Lange et al. does not contain a sufficient teaching that the claimed result would be achieved.*

According to the Examiner, “Lange et al. at col. 4, lines 5-9, clearly teach that the reference primer is clearly suitable ‘as a primer for adhering adhesives to substrates’, with no restrictions whatsoever on the type of adhesive used.” (See Office Action mailed October 28, 2005; ¶ 3.) Applicants respectfully traverse and submit that the cited passage from Lange et al. must be considered in its context. When determining what Lange et al. suggest, one of ordinary

Application No.: 10/689,172

Case No.: 58683US003

skill in the art would at least consider the entire passage, i.e., "The excellent adhesion of the coating to the substrate and the adhesive of the test tape also demonstrates the utility of the coating as a primer for adhering adhesives to substrates, such as polymeric substrates, e.g., polyester films." (Lange et al., col. 4, lines 5-9 (emphasis added).)

Furthermore, one of ordinary skill in the art would realize, as the Examiner has acknowledged, that Lange et al. fail to describe any adhesive other than the specific adhesive of the test tape used. (See Office Action mailed May 25, 2005; ¶ 12.) Applicants note that, in contrast to the adhesives of the present invention, the adhesive of Lange et al. contains greater than 3% by weight acrylic acid. (See Decl. of Robert G. Murray, filed August 18, 2005, and represented in the Evidence Appendix.)

While one of ordinary skill in the art might infer that Lange et al.'s statement was broad enough to encompass adhesives other than the specific "adhesive of the test tape," Applicants respectfully submit that one of ordinary skill in the art, reading Lange et al. in its entirety, would also recognize that such a sweeping interpretation is supported solely by a result achieved with a single adhesive tape applied to a single substrate. Thus, any broad interpretation of this phrase in Lange et al. would be qualified by this knowledge.

Applicants respectfully submit that these factors would detract from Lange et al.'s power to suggest solutions to an artisan of ordinary skill. Thus, at best, Lange et al. might pique a scientist's curiosity to investigate further, but the disclosure of Lange et al. does not contain a sufficient teaching that the claimed result would be achieved. Such an "obvious to try" situation must not be equated with obviousness under 35 U.S.C. § 103(a). (See, e.g., Gillette Co. v. S.C. Johnson & Son, Inc., 919 F.2d 720, 725, 16 USPQ2d 1923, 1928 (Fed. Cir. 1990).)

B. EP '756 clearly and unambiguously steers one of ordinary skill in the art to the use of primers containing nanoparticles modified by ambifunctional silanes, rather than primers consisting essentially of nanoparticles.

In the Advisory Action mailed January 6, 2006, the Examiner noted that Applicants had overcome the 35 USC 103 rejections which partially rely on EP 0 372 756 (EP '756). Although Applicants acknowledge with appreciation the Examiner's position regarding EP '756; Applicants submit that EP '756 remains highly relevant as it clearly and unambiguously teaches away from the present invention. A reference such as EP '756 teaches away when a person of ordinary skill in the art, upon reading the reference, would be "led in a direction divergent from

Application No.: 10/689,172

Case No.: 58683US003

the path that was taken by the applicant.” (*In re Haruna*, 249 F.3d 1327, 1335, 58 U.S.P.Q.2d 1517, 1552 (Fed. Cir. 2001) (quoting *Tec Air, Inc. v. Desno Mfg. Mich. Inc.*, 192 F.3d 1353, 1360, 52 USPQ2d 1294, 1298 (Fed. Cir. 1999).) Therefore, although the Examiner has rejected claims 1-11 and 29-37 as being unpatentable over Lange et al. individually, the limited persuasive power of Lange et al. must be weighed against that of EP ‘756, as their disclosures are in conflict.

EP ‘756 describes a primer layer for pressure-sensitive and cold-seal adhesives. The primer comprises a continuous gelled or hydrolyzed network of inorganic particles. (See page 2, lines 40-44.) EP ‘756 repeatedly and explicitly states that the gelled network of nanoparticles must contain ambifunctional silane. (See, e.g., page 2, lines 40-44 (“The network contains a specified amount of a particular ambifunctional silane”) and lines 50-51 (“The primer layer comprises a continuous network of inorganic particles ... containing an ambifunctional silane”; page 3, lines 22-23 (“The network must contain specified ambifunctional silane”) and lines 49-50 (“A specified adhesion promoting effective amount of an ambifunctional silane must be present in or on the gelled network”); and page 5, lines 23-26 (“The ambifunctional silane is present as from 0.1% to 20% by weight of the solids content of the gelled particulate layer”).)

Thus, EP ‘756 expressly distinguishes the nanoparticles of its primer from the nanoparticles of Lange et al. in that the nanoparticles of EP ‘756 must contain ambifunctional silane. Furthermore, EP ‘756 describes the role of the ambifunctional silane as providing multiple reactive species such that one reactive species can react with the nanoparticle and the other reactive species can react with one of the layers in contact with the primer. (See page 5, lines 23-33.) Such nanoparticles are expressly excluded from Applicants’ definition of a primer that “consists essentially of nanoparticles.” (See, e.g., Specification page 11, lines 20-23.)

Applicants respectfully submit that, in contrast to the limited persuasive power of a broad interpretation of Lange et al.’s assertion, which is based on a single adhesive tape, the persuasive power of EP ‘756 is enhanced by experimental results “show[ing] that Sol-gel/corona constitutes a functional primer for adhesives over a range of film substrate types and adhesive types” (page 8, lines 31-32). (See also, EP ‘756 at Examples 1-4.)

Application No.: 10/689,172

Case No.: 58683US003

C. The Examiner has failed to establish the requisite reasonable expectation of success, and for at least this reason, the rejection should be reversed.

In summary, even in a rejection based solely on Lange et al., the Patent Office must consider the teachings of both Lange et al. and EP '756. The persuasive power of these conflicting references must be assessed, without the benefit of hindsight or Applicants' disclosure. Ultimately, although absolute predictability is not required, a reasonable expectation of success is necessary to show obviousness. (See, e.g., Gillette Co. v. S.C. Johnson & Son, Inc., 919 F.2d 720, 724, 16 USPQ2d 1923, 1928 (Fed. Cir. 1990) (citing In re Farrell, 853 F.2d 894, 903-04, 7 USPQ2d, 1673, 1681 (Fed. Cir. 1988).)

Applicants respectfully submit that no such reasonable expectation has been established. Upon weighing each of the conflicting references for its power to suggest solutions to an artisan of ordinary skill, it is clear that the broad interpretation given to the statement of Lange et al. might, at best, pique a scientist's curiosity to investigate further, but the disclosure of Lange et al. does not contain a sufficient teaching that the claimed result would be achieved. In contrast, the disclosure of EP '756 clearly and unambiguously steers one of ordinary skill in the art to the use of primers containing nanoparticles modified by ambifunctional silanes, rather than primers consisting essentially of nanoparticles. That is, EP '756 would lead one of ordinary skill in a direction divergent from the path that was taken by the applicant.

For at least these reasons, the rejection of claims 1-11 and 29-37 under 35 USC § 103(a) as purportedly being unpatentable over Lange et al. (US Patent No. 4,816,333) is unwarranted, and Applicants respectfully request that this rejection be reversed.

II. Claims 6 and 32 stand rejected under 35 U.S.C. § 103(a) as purportedly being unpatentable over Lange et al., in view of Melancon et al. (US 2003/0152768 A1).

Melancon et al. appears to be cited solely for its description of silicon polyurea based adhesives with reference to pending claims 6 and 32. (See Office Action mailed May 25, 2005; ¶ 12.) Applicants respectfully submit that the Examiner has failed to show how Melancon et al. overcome the deficiencies of Lange et al. as discussed above. For at least these reasons, the rejection of claims 6 and 32 under 35 USC § 103(a) as purportedly being unpatentable over Lange et al. (US 4,816,333) in view of Melancon et al. (US 2003/0152768) is unwarranted and Applicants respectfully request that this rejection be reversed.

Application No.: 10/689,172

Case No.: 58683US003

CONCLUSION

For the foregoing reasons, appellants respectfully submit that the Examiner has erred in rejecting this application. Please reverse the Examiner on all counts.

Respectfully submitted,

June 4, 2007
Date

By: Thomas M. Spielbauer
Thomas M. Spielbauer, Reg. No.: 58,492
Telephone No.: 651-736-9814

Office of Intellectual Property Counsel
3M Innovative Properties Company
Facsimile No.: 651-736-3833

Application No.: 10/689,172

Case No.: 58683US003

CLAIMS APPENDIX

1. (Previously Presented) An adhesive article comprising:
 - (a) a first substrate comprising a first major surface;
 - (b) a first adhesive layer, wherein the first adhesive layer comprises no more than 3% by weight acrylic acid repeat units; and
 - (c) a first primer layer interposed between at least a portion of the first major surface of the substrate and at least a portion of the first adhesive layer, wherein the first primer consists essentially of nanoparticles.
2. (Original) The adhesive article of claim 1, wherein the first substrate is untreated.
3. (Original) The adhesive article of claim 1, wherein the first substrate comprises a polymeric film.
4. (Original) The adhesive article of claim 1, wherein the first substrate comprises a foam.
5. (Previously Presented) The adhesive article of claim 4, wherein the foam comprises a polymer selected from the group consisting of acrylic, polyethylene, ethylene vinyl acetate, and combinations thereof.
6. (Previously Presented) The adhesive article of claim 1, wherein the first adhesive layer comprises at least one of silicone polyurea and acrylate.
7. (Original) The adhesive article of claim 1, wherein the nanoparticles have a maximum cross-sectional dimension of no more than 20 nanometers.
8. (Previously Presented) The adhesive article of claim 1, wherein the nanoparticles are selected from the group consisting of silica, ceria, iron oxide, and combinations thereof.

Application No.: 10/689,172

Case No.: 58683US003

9. (Original) The adhesive article of claim 1, wherein the nanoparticles are surface modified.
10. (Previously Presented) The adhesive article of claim 1, further comprising a second primer layer interposed between at least a portion of the second major surface of the first substrate and at least a portion of a second adhesive layer.
11. (Previously Presented) The adhesive article of claim 1, further comprising a second primer layer interposed between at least a portion of a first major surface of a second substrate and at least a portion of the first adhesive layer.

Claims 12-28 (Cancelled)

29. (Previously Presented) A method of bonding an adhesive layer to a substrate comprising:
- (a) interposing a primer consisting essentially of nanoparticles between a first major surface of the substrate and a first major surface of the adhesive layer, wherein the adhesive layer comprises no more than 3% by weight acrylic acid repeat units;
 - (b) adhering at least a portion of the first major surface of the substrate to the primer;
- and
- (c) adhering at least a portion of the first major surface of the adhesive layer to the primer.
30. (Original) The method of claim 29, wherein the substrate is a polymeric film.
31. (Previously Presented) The method of claim 30, wherein the substrate comprises a polymer selected from the group consisting of polyolefins, polyesters, polyimides, polystyrenes, acrylics, polyacrylates, polymethacrylates, polymethylmethacrylates, polyurethanes, urethane acrylate polymers, epoxy acrylate polymers, polyacetals, polycarbonate, polysulfone, cellulose acetate butyrate, polyvinyl chloride, and combinations thereof.

Application No.: 10/689,172

Case No.: 58683US003

32. (Previously Presented) The method of claim 29, wherein the adhesive comprises at least one of silicone polyurea and acrylate.
33. (Original) The method of claim 29, wherein the nanoparticles have a maximum cross-sectional dimension of no more than 20 nanometers.
34. (Previously Presented) The method of claim 29, wherein the nanoparticles are selected from the group consisting of silica, ceria, iron oxide and combinations thereof.
35. (Original) The method of claim 29, wherein the nanoparticles are surface modified.
36. (Original) The method of claim 29, wherein (b) comprises providing a primer solution comprising the nanoparticles and applying the primer solution to at least a portion of the first major surface of the substrate; and (c) comprises contacting at least a portion of the primed portion of the first major surface of the substrate with at least a portion of the first major surface of the adhesive layer.
37. (Previously Presented) The method of claim 29, wherein (c) comprises providing a primer solution comprising the nanoparticles and applying the primer solution to at least a portion of the first major surface of the adhesive layer; and (b) comprises contacting at least a portion of the primed portion of the first major surface of the adhesive layer with at least a portion of the first major surface of the substrate.
38. (Cancelled)

Application No.: 10/689,172

Case No.: 58683US003

EVIDENCE APPENDIX

(A) Declaration under 37 C.F.R. § 1.132 by Robert G. Murray.

- First submitted to the USPTO with Applicants' Amendment and Response under 37 C.F.R. § 1.111, mailed August 18, 2007.
- Entry of the evidence is inferred from the Examiner's consideration and comments regarding the Murray Declaration on page 3 of the Office Action mailed October 28, 2005.

(B) EP 0 372 756

- First cited to the USPTO in an IDS mailed January 15, 2004.
- Entry of the evidence is shown by the initialed IDS form included with the Office Action mailed May 25, 2005.
- Entry of the evidence can also be inferred from the Examiner's reliance on EP 0 373 756 is formulating a rejection under 35 U.S.C. § 103 set forth in paragraph 12 of the Office Action mailed May 25, 2005.

JUN 05 2007

Application No.: 10/689,172

Case No.: 58683US003

(A) Murray Declaration

32692

Customer Number

Patent
Case No.: 58683US003

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor: LUNSFORD, DUANE A.

DUE DATE(S)

ATTORNEY

DOCKETED

Application No.: 10/689172

Group Art Unit: 1771

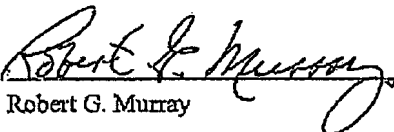
Filed: October 20, 2003

Examiner: Daniel R. Zirker

Title: ADHESIVE ARTICLES INCLUDING NANOPARTICLE PRIMER AND
METHODS FOR PREPARING SAMEDECLARATION UNDER 37 C.F.R. § 1.132

I, Robert G. Murray, declare:

1. I have been an employee of 3M Company since September 29, 1969.
2. I had product control responsibility for 3M's Scotch Brand Magic transparent tape from about 1979 to 1983.
3. I have continued to work on processes associated with the manufacture of the 3M's Scotch Brand Magic transparent tape adhesive from 1983 to the present.
4. From at least 1969 until the present, the adhesive used with 3M's Scotch Brand Magic transparent tape contained greater than 3% by weight acrylic acid.
5. The undersigned declares further that all statements made herein of his own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful, false statements and the like are punishable by a fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful, false statements may jeopardize the validity of the application or any patent issuing thereon.


Robert G. Murray8.17.2005
Date

Application No.: 10/589,173

Case No.: 58683U5003

(E) EP 0 372 756

(B) EP 0 372 756

Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number: **0 372 756 B1**

⑫

EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification: 29.12.93 ⑤① Int. Cl.⁵: **C09J 7/02**

②① Application number: 89312167.3

②② Date of filing: 23.11.89

⑤④ Pressure-sensitive article with priming layer.

③⑦ Priority: 05.12.88 US 279974

④③ Date of publication of application:
13.06.90 Bulletin 90/24

④⑧ Publication of the grant of the patent:
29.12.93 Bulletin 93/52

⑤④ Designated Contracting States:
DE ES FR GB IT

⑤⑥ References cited:
EP-A- 0 301 827
US-A- 4 196 254

⑦③ Proprietor: MINNESOTA MINING AND MANU-
FACTURING COMPANY
3M Center,
P.O. Box 33427
St. Paul, Minnesota 55133-3427(US)

⑦② Inventor: Strobel, Mark A. Minnesota Mining
and Manufacturing Co
2501 Hudson Rd
P.O. Box 33427
St. Paul Minnesota 55133-3427(US)
Inventor: Corn, Stewart H. Minnesota Mining
and Manufacturing
2501 Hudson Rd

P.O. Box 33427
St. Paul Minnesota 55133-3427(US)
Inventor: Boston, David D. Minnesota Mining
and Manufacturing
2501 Hudson Rd
P.O. Box 33427
St. Paul Minnesota 55133-3427(US)
Inventor: Woo, Edward J. Minnesota Mining
and Manufacturing
2501 Hudson Rd
P.O. Box 33427
St. Paul Minnesota 55133-3427(US)

⑦④ Representative: Ballile, Iain Cameron et al
c/o Ladas & Parry
Altheimer Eck 2
D-80331 München (DE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Rank Xerox (UK) Business Services
B. 10/3.6/3.3.11

EP 0 372 756 B1

EP 0 372 756 B1

Description

BACKGROUND OF THE INVENTION

6 1. Field of the Invention

The present invention relates to a novel type of priming layer for pressure-sensitive adhesive articles. The invention particularly relates to film or sheet materials having a cold-seal or pressure-sensitive adhesive layer and the primer layer of the present invention.

10

2. Background of the Art

Priming layers are often used when bonding or coating two different materials together. The objective of the priming layer (or prime) is to control the level of adherence of one material to another. Ordinarily the priming layer is used to increase the bond strength between two layers.

Where a coating is applied to a substrate and the composition of the coating does not have a natural affinity for the substrate, a primer layer is often used. Materials such as polyethylene terephthalate or polyolefins have well known problems in having coatings adhered thereto. In the photographic art, it's almost essential that priming layers be used, such as described in U.S. Patent Nos. 3,343,840; 3,495,984; and 3,788,858. European Patent Publication No. 0,301,827 published after the priority date of the subject patent and accordingly only available as a piece of relevant prior art for the purposes of Articles 54(3) and 54(4) EPC in respect of some only of the designated states of the subject patent discloses the use of a continuous gelled or hydrolyzed coating of particular inorganic oxides to form a subbing layer for photographic elements. These primer layers were found to provide good bonding strength for photosensitive silver halide layers, particularly those with gelatin binders, and were also found to provide good antistatic properties. The reference describes the use of ambifunctional silane coupling agents in the continuous network of particles to improve the wet development strength of the primer layer.

United States Patent No. 4,196,254 (Puskadl) discloses a pressure-sensitive adhesive tape having a polyolefin, polyester or metal foil backing and an acrylate pressure-sensitive adhesive layer firmly adhered to the backing through a primer layer comprising a primer composition consisting essentially of an intimate mixture of a primary amino-functional trialkoxy silane and a particular carboxylated polymer component having an affinity for the acrylate adhesive.

Many other combinations of coatings and substrates require the use of primer layers which are particularly suitable for the exact combination of materials to be adhered. Pressure-sensitive adhesives are known to need primers for certain surfaces (e.g., U.S. Patent No. 3,991,002) and many other polymer coatings also need unique priming systems (e.g., U.S. Patent No. 4,181,766).

SUMMARY OF THE INVENTION

The present invention relates to pressure-sensitive or cold-seal adhesive elements having a substrate, a primer layer on said substrate, and a pressure-sensitive or cold-seal adhesive layer on said primer layer, each primer layer having a specified thickness and comprising a continuous gelled or hydrolyzed network of inorganic particles, preferably inorganic oxide particles. The network contains a specified amount of a particular ambifunctional silane.

45

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to pressure-sensitive or cold-seal adhesive elements. These elements comprise a substrate having a primer layer on at least one surface of the substrate and a pressure-sensitive or cold-seal adhesive layer on at least one primer layer. The primer layer comprises a continuous gelled network of inorganic particles, preferably inorganic oxide particles, containing an ambifunctional silane.

Pressure-sensitive adhesives are art recognized as a standard class of materials. These are adhesives which in dry (substantially solvent free except for residual solvent) form are aggressively and permanently tacky at room temperature (e.g., 15 to 25 °C) and firmly adhere to a variety of dissimilar surfaces upon mere contact without the need for more than manual pressure. They require no activation by water, solvent or heat in order to exert a strong adhesive holding force towards such materials as paper, cellophane, glass, wood and metals. They have a sufficiently cohesive holding and elastic nature so that, despite their aggressive tackiness, they can be handled with the fingers and removed from smooth surfaces without

EP 0 372 756 B1

leaving a substantial residue (cf. Test Methods for Pressure-Sensitive Tapes, 6th Ed., Pressure Sensitive Tape Council, 1953). Pressure-sensitive adhesives and tapes are well known, and the wide range and balance of properties desired in such adhesives has been well analyzed (cf. U.S. Patent 4,374,883; and "Pressure-Sensitive Adhesives" in Treatise on Adhesion and Adhesives Vol. 2, "Materials", R.I. Patrick, Ed., Marcel Dekker, Inc., N.Y., 1969). The various materials and compositions useful as pressure-sensitive adhesives are available commercially and are thoroughly discussed in the literature (e.g., Houwink and Salomon, *Adhesion and Adhesives*, Elsevier Publ. Co., Amsterdam, Netherlands, 1967; Handbook of Pressure-Sensitive Adhesive Technology, Donates Satas, Ed., VanNostrand Reinhold Co., N.Y., 1982).

Pressure-sensitive adhesives are generally chemically composed of rubber-resin materials, acrylic resins, polyurethane resins, silicone resins, and the like. Among the various patent literature describing compositions and improvements in pressure-sensitive adhesive formulations are U.S. Reissue Patent No. 24,906; U.S. 2,652,351; U.S. 3,740,366; U.S. 3,299,010; U.S. 3,770,708; U.S. 3,701,758; U.S. 3,922,464; U.S. 3,931,087; U.S. 4,012,560; U.S. 4,077,926; U.S. 4,387,172; U.S. 4,418,120; U.S. 4,629,663; and the like. These classes of rubber resin, acrylic, silicone, and polyurethane pressure-sensitive adhesives as well as any other pressure-sensitive adhesives are generally useful in the present invention.

A cold seal adhesive is a material that under pressure alone will form a strong bond and for example, may comprise an uncrosslinked copolymer of (a) 10 to 50 weight percent of acrylonitrile and (b) 50 to 90 weight percent of at least one of butadiene and isoprene, said copolymer having a Mooney viscosity of from 30 to 95, and said adhesive copolymer layer having a water contact angle of at least 20°. A cold-seal adhesive is pressure-sensitive in a sense (it bonds under pressure), but differs from the conventional pressure-sensitive adhesive in that cold-seal adhesives are not tacky at room temperature.

The substrate of the invention bears a coating comprising a continuous gelled network of inorganic metal oxide particles. The network must contain specified ambifunctional silane. The particles preferably have an average primary particle size of less than 50 or 20 nm. As used herein, the term "continuous" refers to covering the surface of the substrate with virtually no straight-line penetrable discontinuities or gaps in the areas where the gelled network is applied. However, the layer may be and usually is porous, without significant straight-line pores or gaps in the layer. The term "gelled network" refers to an aggregation of colloidal particles linked together to form a porous three-dimensional network. Generally all of or the majority of linkages are from the material of the particles to each other or to the silane additive, but some binder such as up to 5% by weight (to the metal oxide) of polymer may also be present. The term "porous" refers to the presence of voids between the inorganic metal oxide particles created by the packing of the metal oxide particles. The term "primary particle size" refers to the average size of unagglomerated single particles of inorganic metal oxide. The term "particle" includes spherical, non-spherical, and fibrillar particulate arrangements. If the ambifunctional silane is added to an aqueous metal oxide sol before coating, then the silane will be hydrolyzed at the positions described as (OR') wherein R' is a hydrocarbyl group such as alkyl, aryl, acalkyl, and alkaryl, substituting hydroxy groups for the (OR') groups. For example, a triethoxysilane will become a trihydroxysilane. In solution with the metal oxide particles, the hydrolyzed silane molecules may associate with the metal oxide particles by "oxane" bonding in a reversible fashion ($\text{SiOH} + \text{HOM}(\text{particle}) \rightleftharpoons \text{Si-O-M}(\text{particle})$). As the solution is dried into a coated layer, it is expected that most of the hydrolyzed silane molecules will become associated with metal oxide particles through "oxane" bonding such that they cannot be washed out of the coating by a simple water wash.

The presence of the silane molecules does not prevent the gelled particle network from gaining cohesive strength, although the time required to gain cohesive strength may be increased.

The coating is of specified thickness and should be thicker than a monolayer of particles. Preferably the coating comprises a thickness equal to or greater than three average particle diameters and more preferably equal to or greater than five particle diameters.

The articles of the invention comprise a substrate which may be transparent, translucent, or opaque to visible light having at least one polymeric or metallic surface, and have formed thereon a coating in the form of a continuous gelled network of inorganic oxide particles. A specified adhesion promoting effective amount of an ambifunctional silane must be present in or on the gelled network. When the coating is applied to transparent substrates to achieve increased light transmissivity, the coated article preferably exhibits a total average increase in transmissivity of normal incident light of at least two percent and up to as much as ten percent or more, when compared to an uncoated substrate, depending on the substrate coated, over a range of wavelengths extending at least between 400 to 900 nm. An increase in light transmission of two percent or more is generally visually apparent and is sufficient to produce a measurable increase in energy transmissivity when the coated substrate is used. An increase in transmissivity is also present at wavelengths into the infrared portion of the spectrum.

EP 0 372 756 B1

The gelled network is a porous coating having voids between the inorganic oxide particles. If the porosity is too small, the antireflectance may be reduced. If the porosity is too large, the coating is weakened and may have reduced adhesion to the substrate. Generally, the colloidal solution from which the gelled network is obtained is capable of providing porosity of 25 to 70 volume percent, preferably 30 to 60 volume percent when dried. The porosity can be determined by drying a sufficient amount of the colloidal solution to provide a dried product sample of 50 to 100 mg and analyzing the sample using a "Quantasorb" surface area analyzer available from Quantachrome Corp., Syosett, NY.

The voids of the porous coating provide a multiplicity of subwavelength interstices between the inorganic particles where the index of refraction abruptly changes from that of air to that of the coating material. These subwavelength interstices, which are present throughout the coating layer, provide a coating which may have a calculated index of refraction (RI) of from 1.15 to 1.40, preferably 1.20 to 1.30 depending on the porosity of the coating. When the porosity of the coating is high, e.g., 70 volume percent or more, lower values for the RI are obtained. When the porosity of the coating is low, e.g., 25 volume percent or less, higher values for the RI are obtained.

The average primary particle size of the colloidal inorganic metal oxide particles is preferably less than about 20 nm. The average primary particle size of the colloidal inorganic metal oxide particles is more preferably less than about 7 nm. When the average particle size becomes too large, the resulting dried coating surface is less efficient as an antireflection coating.

The average thickness of the dried coating is from 30 to 1,000 nm, more preferably 80 to 500 nm and most preferably between 90 and 200 nm. Such coatings provide good antistatic properties. When the coating thickness is too great, the coating has reduced adhesion and flexibility and may readily flake off or form powder under mechanical stress.

Articles such as transparent sheet or film materials may be coated on a single side or on both sides to increase light transmissivity, the greatest increase being achieved by coating both sides.

The process of coating the layer of the present invention comprises coating a substrate with a solution of colloidal inorganic metal oxide particles (and preferably the silane at this point), the solution preferably containing at least 0.2 or 0.5 to 15 weight percent of the particles, the particles preferably having an average primary particle size less than 50 or 20 nm, more preferably less than 7 nm, and drying the coating at a temperature less than that which degrades the substrate, preferably less than 200 °C, more preferably in the range of 80 to 120 °C. The coating provides the substrate with an average reduction in specular reflectance of at least two percent over wavelengths of 400 to 900 nm.

Coating may be carried out by standard coating techniques such as bar coating, roll coating, knife coating curtain coating, rotogravure coating, spraying and dipping. The substrate may be treated prior to coating to obtain a uniform coating or to promote adhesion using techniques such as corona discharge, plasma, flame treatment, or other oxidizing processes. With some substrates, treatment is particularly desirable for good adhesion. The specified ambifunctional silane may be added before, during or after coating. It is preferred to add the silane to the coating mixture before coating. If the silane is added after the "gelled network" has been coated and dried, it should be added from a water-containing solution, so that the silane will be in its hydrolyzed form.

The colloidal inorganic oxide solution, e.g., a hydrosol or organosol, is applied to the substrate of the article to be coated and dried at a moderately low temperature, generally less than 200 °C, preferably 80-120 °C, to remove the water or organic liquid medium. The coating may also be dried at room temperature, provided the drying time is sufficient to permit the coating to dry completely. The drying temperature should be less than at which the substrate degrades. The resulting coating is hygroscopic in that it is capable of absorbing and/or rehydrating water, for example, in an amount of up to 15 to 20 weight percent, depending on ambient temperature and humidity conditions.

The colloidal inorganic oxide solution utilized in the present invention comprises finely divided solid inorganic metal oxide particles in a liquid. The term "solution" as used herein includes dispersions or suspensions of finely divided particles of ultramicroscopic size in a liquid medium. The solutions used in the practice of this invention are clear to milky in appearance. Inorganic metal oxides particularly suitable for use in the present invention are those in which the metal oxide particles are negatively charged, which includes tin oxide (SnO₂), titania, antimony oxide (Sb₂O₃), silica, and alumina-coated silica as well as other inorganic metal oxides of Groups III and IV of the Periodic Table and mixtures thereof. The selection of the inorganic metal oxide is dependent upon the ultimate balance of properties desired. Inorganics such as silicon nitride, silicon carbide, and magnesium fluoride when provided in sol form are also useful.

The colloidal coating solution preferably contains 0.2 to 15 weight percent, more preferably 0.5 to 8 weight percent, colloidal inorganic metal oxide particles. At particle concentrations of about 15 weight percent, the resulting coating may have reduced uniformity in thickness and exhibit reduced adhesion to the

EP 0 372 756 B1

substrate surface. Difficulties in obtaining a sufficiently thin coating to achieve increased light transmissivity and reduced reflection may also be encountered at concentrations above about 15 weight percent. At concentrations below 0.2 weight percent, process inefficiencies result due to the large amount of liquid which must be removed and antireflection properties may be reduced.

5 The thickness of the applied wet coating solution is dependent on the concentration of inorganic metal oxide particles in the coating solution and the desired thickness of the dried coating. The thickness of the wet coating solution is such that the resulting dried coating thickness is from 30 to 1,000 nm, preferably from 80 to 500 nm thick, most preferably 90 to 200 nm thick.

10 The coating solution may also optionally contain a surfactant to improve wettability of the solution on the substrate, but inclusion of an excessive amount of surfactant may reduce the adhesion of the coating to the substrate. Examples of suitable surfactants include "Tergitol" TMN-6 (Union Carbide Corp.) and "Triton" X-100 (Rohm and Haas Co.). Generally the surfactant can be used in amounts of up to 0.5 weight percent of the solution.

15 The coating solution may optionally contain a very small amount of polymeric binder, particularly a hydrophilic polymer binder, to improve scratch resistance, or to reduce formation of particulate dust during subsequent use of the coated substrate. Useful polymeric binders include polyvinyl alcohol, polyvinyl acetate, gelatin, polyesters, polyamides, polyvinyl pyrrolidone, copolyesters, copolymers of acrylic acid and/or methacrylic acid, and copolymers of styrene. The coating solution can contain up to 5 weight percent of the polymeric binder based on the weight of the inorganic metal oxide particles. Useful amounts of polymeric binder are generally in the range of 0.1 to 5 weight percent to reduce particulate dust. These binders can reduce some of the beneficial properties (e.g., antistatic properties) of the coatings if used, so that they are not most preferred.

20 The ambifunctional silane is present as from 0.1% to 20% by weight of the solids content of the gelled particulate layer. Preferably the ambifunctional silane is present as from at least 1.0 by weight of the solids content of the particulate layer. More preferably the silane is present as 2.0 to 15% by weight of the solids content of the particulate layer, and most preferably as 3 to 10% by weight.

25 The term ambifunctional silane means that the compound has reactive silanes on one end of the molecule and a different reactive species capable of reacting with a photographic hardener for gelatin or with oxidized functional groups (e.g., hydroxyl or preferably carboxylic acid) on the polymeric surfaces which are in contact with the inorganic oxide layer. This second functionality enables the compound to react with the inorganic particle (through the silane group) and also react with the oxidized functional group (or reacting with an additive which also reacts with the main polymer) and/or with oxidized or oxygen containing groups on the substrate. Amongst the preferred second functional groups on the compound are amino groups and epoxy (e.g., glycidyl) groups. The second functionality may be present as a single functional moiety or may be present as a multiple number of such groups.

A formula that is used to represent the ambifunctional silanes of the present invention is



30 wherein

R' is alkyl or aryl,

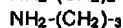
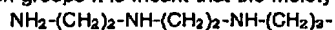
R is an organic group with (n + 1) external bonds or valences,

n is 0, 1 or 2, and

35 Q is a moiety reactive with photographic hardeners, oxidized functionalities or directly with gelatin (e.g., alpha-amino acids).

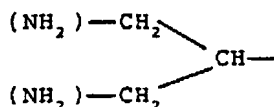
Preferably R' is alkyl of 1 to 10 carbon atoms and most preferably 1 to 4 carbon atoms. R is preferably an aliphatic or aromatic bridging group such as alkylene, arylene, alkarylene, or aralkylene which may be interrupted with ether linkages (oxygen or thioethers), nitrogen linkages, or other relatively inert moieties. More preferably R is alkylene of 1 to 12 carbon atoms, preferably 2 to 8 carbon atoms, with n equal to 1. Q is preferably epoxy, or amino, primary or secondary, more preferably primary amino.

40 Where previously indicated that the second functional group may be present as a multiple number of such groups it is meant that the moiety (Q)_n-R- may include moieties such as



45 (NH₂)₂-CH-CH₂- and

EP 0 372 756 B1



5

The substrates of the invention may comprise any material having at least one polymeric surface which is to be used as the major surface of the substrate. The substrates preferably have an oxygen containing functional moiety on its surface. This moiety may be present as a result of the chemical nature of the surface or as a result of oxygenating treatment of the surface as by corona, plasma, flame treatment, etc. The preferred oxygen containing moieties are hydroxyl and carboxyl, particularly carboxylic acid. Ester groups, aldehyde groups and silanols are also useful moieties. The groups may be part of the substantive base or a coating thereon (as on coated paper). Some polymeric film surfaces contain small amounts of active functional groups (including oxygen containing groups) due to the presence of particular end groups on the polymers (e.g., polyethyleneterephthalate has -COOH end groups) or as a result of incomplete reaction of the monomers (e.g., incomplete esterification of cellulose triacetate, CTA). In these cases the density of surface functional groups tends to be insufficient by itself to gain good adhesion to the sol-gel coatings of this invention. Thus, polyethyleneterephthalate and cellulose triacetate should be corona treated prior to application of the sol-gel coating composition for attaining the best results. Many other film surfaces normally contain sufficient oxygen functional groups to enable good adhesion to the primer of the invention without any corona treatment. Films such as polycarbonates are noteworthy in this regard. Esters may be subjected to hydrolysis or energy treatment to produce -COOH or -OH groups on the surface.

Supports which can be used include films of metal, or metal coated polymers, or synthetic polymers such as polyalkyl acrylate or methacrylate, polystyrene, polyvinyl chloride, partial formulation polyvinyl alcohol, polycarbonate, polyalkylenes, polyolefins, polyesters such as polyethylene terephthalate, and polyamides, films of cellulose derivatives such as cellulose nitrate, cellulose acetate, cellulose triacetate, and cellulose acetate butyrate, paper covered with α -olefin polymers or gelatin (a natural polymer), for example, and synthetic papers made of polystyrene; that is, any transparent or opaque support. Primed polymeric substrates are also useful but less preferred since the sol-gel coating is a primer, including, but not limited to, gelatin-primed polymers (e.g., gelatin on poly(ethylene terephthalate)), and poly(vinylidene chloride) copolymers on polyester. Other primers such as aziridines, acrylates, and melamine-formaldehyde are also useful. This includes polymeric materials loaded with pigments and particulates such as titania to improve the white background appearance of the element.

35

EXAMPLES 1 & 2

Samples of sol-gel coated cellulose acetate (CA) and biaxially oriented polypropylene (BOPP) were prepared as follows: Thermally extruded, biaxially oriented 50-micrometer thick, 15-cm wide polypropylene film (Example 1) and the glossy side of extruded 40-micrometer thick, 15-cm wide cellulose acetate (Example 2) were corona treated at 25° C in ambient air at an energy level of 0.7 J/cm² (23 m/min film velocity at a corona power of 2250 W). The treated films were then overcoated with the sol-gel composition using an air-knife coater and dried for about 1 minute at 65° C to achieve a dry coating thickness of about 260 nm. The sol-gel composition consisted of 4% Naico 2326 colloidal silica, 0.36% aminopropyltriethoxysilane coupling agent, and 0.03% Triton-X-100 surfactant, in water. Also, non-corona treated samples of the same substrates were coated with the sol-gel composition.

Acrylate Adhesive Coating & Testing

The sol-gel primed substrates and unprimed control films were coated with a latex acrylate adhesive consisting of neutralized 95:5 Isooctylacrylate: acrylic acid copolymer emulsion dispersed in water. After evaporation of the water to leave an adhesive layer about 20 micrometers thick, the coated products were converted to roll form, that is, to rolls of PSA tape. The adhesive-coated, sol-gel-coated substrates were then conditioned at ca. 20° C and 50% r. h. for 24 hours prior to adhesion testing.

The adhesive surface of each sample was then placed in contact with an anodized aluminum plate and the film rolled down with a 1-kg roller to insure intimate contact. When the film is stripped off at 90° to the aluminum plate at a rate of about 230 cm/min, the removal force should be greater than for an untreated, uncoated control film. It is necessary that the predominant mode of adhesive failure be cohesive in the

EP 0 372 758 B1

acrylate adhesive ("split") at peel forces greater than ca. 1.1 kg/cm rather than separated from the film and adhering to the aluminum plate ("adhesive transfer" or "sol-gel transfer").

Those samples showing acceptable performance ("split") after initial testing were then subjected to heat aging for 11 days at 50° C prior to retesting by the method described above. The results of adhesion testing are given in two parts: the bond strength in kg/cm and the mode of adhesion failure. In addition to the two corona treated, sol-gel primed examples, also listed are six comparative controls consisting of the two untreated base films, the two films coated with sol-gel without a prior air-corona treatment, and the two films treated with an air corona but without an sol-gel overcoating.

	<u>initial (Kg/cm)</u>	<u>after heat aging*</u>
10		
<u>Example 1</u>		
Sol-gel-on-BOPP	1.4-1.5, split	1.25-1.5, split
15		
<u>Example 2</u>		
Sol-gel-on-CA	1.4-1.5, split	1.15-1.4, split
<u>Controls</u>		
Untreated BOPP	0.3-0.5, adhesive transfer	
20		
Untreated CA	0.5-0.7, adhesive transfer	
Sol-gel-on-untreated-BOPP	0, sol-gel transfer	
25		
Sol-gel-on-untreated-CA	0.35-1.55, sol-gel transfer	
air-corona-treated BOPP (no sol-gel)	0.35-0.6, adhesive transfer	
30		
air-corona-treated CA	0.6-1.1, adhesive transfer	
35		
* - 11 days at 50° C		

EXAMPLES 3 & 4

40 Preparation of Primed Substrates: The substrates listed below were corona treated at 25°C in air at a power level of 0.7/J/cm² (800W, at 15m/min). The treated film was then overcoated with an sol-gel coating mixture, using a draw-down technique with a #4 wirewound rod. The sol-gel coating mixture consisted of: 4% Nalco 232B colloidal silica, 0.38% aminopropyltriethoxysilane, and 0.03% Triton X-100 in water. The silica coating was then cured in a counterflow oven for 2 min. at 100°C.

45 Example 3

Natural Rubber (isoprene/polyterpene) adhesive (3M #610) tape-pull adhesion test: Half of a 2.5cm X 10cm piece of adhesive tape consisting of a natural rubber (isoprene/polyterpene) adhesive coated onto a cellophane backing was affixed to the primed film surface using a plastic card. Then, while holding the film on a flat surface, the tape was pulled at about 120° with sufficient force to cause adhesive failure. Adhesion of primer to both substrate and adhesive was considered excellent if the natural rubber adhesive was stripped from its cellophane backing and onto the primer sol-gel.

The tape-pull test described above was applied to the various sol-gel/corona primed films listed below. In all cases, the natural rubber adhesive stripped to the sol-gel coating.

EP 0 372 756 B1

Film Type

	PE	polyethylene
	cast PP	polypropylene
5	BOPP	biaxially-oriented polypropylene
	PET	polyethyleneterephthalate
	PMMA	polymethylmethacrylate
	Polycarbonate	
	Cellulose acetate	
10	Nylon-6	
	Silicone release film	
	PVC	polyvinylchloride
	PVF ₂	polyvinylidenedifluoride (-CH ₂ CF ₂) _n

15 Example 4.

Cold Seal (acrylonitrile/butadiene) adhesive: Adhesion was tested according to the following method: The primed film surface was placed in contact with an anodized aluminum plate bearing a butadiene/acrylonitrile cold seal adhesive, rolled six times with a 2 kg roller, and allowed to remain at room temperature conditions for 24 hours. A free end of the film was then doubled back on itself at 180° and
20 stripped away at about 230 cm/min. The force to cause adhesive failure is measured in kg/cm.

The test method for cold seal adhesive was applied as above. Sol-gel/corona was compared to untreated film, corona only, and sol-gel only. Breaking forces are in kg/cm.

26

Film Type	Sol-Gel/corona	Untreated	Sol-Gel only	corona only
PE	>0.8	.02	0	0.2
PVF ₂	>0.8	.02	0	0.25

30

The above results show that Sol-gel/corona constitutes a functional primer for adhesives over a range of film substrate types and adhesive types. It differs from traditional primers in that its usefulness derives from its high surface area and microporosity. It also differs from traditional priming methods because it is applied from aqueous medium. Furthermore, it is especially amenable to the use of waterborne adhesive latexes,
35 promoting both adhesion and coatability of the latex.

Claims

- 40 1. A pressure-sensitive or cold-seal adhesive element comprising a substrate having on at least one surface thereof a primer layer said primer layer having an average thickness of between 30 and 1000 nm, and adhered to said primer layer a pressure-sensitive or cold-seal layer, said primer layer comprising a continuous gelled network of inorganic particles containing an ambifunctional silane in an adhesion promoting effective amount of from 0.1% to 20% by weight of the solids content of said gelled particulate primer layer, said ambifunctional silane being represented by the formula:

46



wherein

50

R¹ is alkyl or aryl,

R is an organic group having n+1 external valences,

n is 1, or 2, and

Q is a moiety reactive with gelatin hardeners, gelatin, carboxyl groups, or hydroxyl groups on organic polymers.

56

2. The element of claim 1 wherein said substrate comprises an organic polymeric film or sheet.
3. The element of any preceding claim wherein said inorganic particles comprise inorganic oxide particles.

EP 0 372 756 B1

4. The element of any preceding claim wherein said inorganic oxide particles are selected from silica, titania, tin oxide and mixtures thereof.
5. The element of any preceding claim where R¹ is alkyl of 1 to 4 carbon atoms, R is a bridging moiety selected from alkylene, arylene, alkarylene, and aralkylene of up to 10 carbon atoms, n is 1, and Q is amino or epoxy.
6. The element of any preceding claim wherein said surface of said substrate has oxygen-containing moieties thereon.

Patentansprüche

1. Haftkleb- oder Kaltsiegelklebelement, umfassend ein Substrat mit mindestens der einen Oberfläche davon als eine Grundierschicht, wobei die Grundierschicht eine mittlere Dicke zwischen 30 und 1.000 nm aufweist, und mit der Grundierschicht verklebt eine Haftkleber- oder Kaltsiegelschicht, wobei die Grundierschicht ein zusammenhängendes geliertes Netzwerk von anorganischen Teilchen aufweist, die ein ambifunktionelles Silan in einer die Haftung fördernden wirksamen Menge von 0,1 % bis 20 Gew.% des Feststoffgehalts der Grundierschicht mit gelierten Feststoffteilchen enthalten, und das ambifunktionelle Silan dargestellt wird durch die Formel:



worin

- R¹ Alkyl oder Aryl ist,
R eine organische Gruppe mit n + 1 externen Valenzen ist,
n 1 oder 2 ist und
Q eine Gruppe ist, die mit Gelatinehärttern reaktionsfähig ist, Gelatine, Carboxylgruppen oder Hydroxylgruppen an organischen Polymeren.
2. Element nach Anspruch 1, bei welchem das Substrat ein organischer polymerer Film oder Folie ist.
3. Element nach einem der vorstehenden Ansprüche, bei welchem die anorganischen Teilchen anorganische Oxidteilchen umfassen.
4. Element nach einem der vorstehenden Ansprüche, bei welchem die anorganischen Oxidteilchen ausgewählt werden aus Silica, Titandioxid, Zinnoxid und deren Mischungen.
5. Element nach einem der vorstehenden Ansprüche, bei welchem R¹ Alkyl mit 1 bis 4 Kohlenstoffatomen ist, R eine brückenbildende Gruppe ist, die ausgewählt wird aus Alkylen, Arylen, Alkarylen und Aralkylen mit bis zu 10 Kohlenstoffatomen, n 1 ist und Q Amino oder Epoxy ist.
6. Element nach einem der vorstehenden Ansprüche, bei welchem die Substratoberfläche Sauerstoff enthaltende Gruppen aufweist.

Revendications

1. Élément adhésif sensible à la pression ou pour soudage à froid, comprenant un substrat sur au moins l'une des surfaces duquel se trouve une couche promotrice d'adhérence, la couche promotrice d'adhérence ayant une épaisseur moyenne d'environ 30 à 1000 nm, une couche sensible à la pression, ou pour soudage à froid, adhérent à la couche promotrice d'adhérence, la couche promotrice d'adhérence comprenant un réseau gélifié continu de particules minérales contenant un silane bifonctionnel, en une quantité à effet promoteur d'adhérence de 0,1 à 20 % en poids par rapport à la teneur en extrait sec de la couche promotrice d'adhérence particulaire gélifiée, le silane bifonctionnel étant représenté par la formule :

EP 0 372 756 B1



dans laquelle R¹ est un radical alkyle ou aryle,

R est un groupe organique ayant n + 1 valences externes,

5 n vaut 1 ou 2, et

Q est un fragment pouvant réagir avec les durcisseurs à base de gélatine, la gélatine, les groupes carboxyle ou encore les groupes hydroxyle se trouvant sur des polymères organiques.

2. Élément selon la revendication 1, dans lequel le substrat comprend un film ou une feuille polymère
10 organique.
3. Élément selon l'une quelconque des revendications précédentes, dans lequel les particules minérales comprennent des particules d'oxydes minéraux.
- 15 4. Élément selon l'une quelconque des revendications précédentes, dans lequel les particules d'oxyde minéral sont choisies parmi la silice, l'oxyde de titane, l'oxyde d'étain et leurs mélanges.
5. Élément selon l'une quelconque des revendications précédentes, dans lequel R¹ est un radical alkyle ayant de 1 à 4 atomes de carbone, R est un fragment pontant choisi parmi l'ensemble comprenant les
20 radicaux alkylène, arylène, alcarylène et aralkylène ayant jusqu'à 10 atomes de carbone,
n vaut 1, et
Q est un radical amino ou époxy.
6. Élément selon l'une quelconque des revendications précédentes, dans lequel la surface du substrat
25 porte des fragments oxygénés.

30

35

40

45

50

55